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ATTN: BOX PCT

Re: Application of Yoshiaki ODA, Kazuhiro YAMAUCHI, Hidenori HANAOKA and Hiroshi SOUDA
**PROCESS FOR THE PREPARATION OF CYCLOPENTADIENYL METAL SALT AND PROCESS FOR
THE PREPARATION OF DERIVATIVE OF CYCLOPENTADIENE USING THE SAME**

Our Reference: Q55095

PCT/JP98/00110, filed January 14, 1998

Dear Sir:

Applicants herewith submit the attached papers for the purpose of entering the National stage under 35 U.S.C. § 371 and in accordance with Chapter II of the Patent Cooperation Treaty. Attached hereto is the application identified above which is a translation of **PCT International Application No. PCT/JP98/00110**, filed **January 14, 1998**, comprising the specification, claims, executed Declaration and Power of Attorney, Notification of Transmittal of Copies of Translation of the International Preliminary Examination Report, International Preliminary Examination Report, Information Disclosure Statement, PTO Form 1449 with references, International Search Report, executed Assignment and PTO Form 1595.

The Government filing fee is calculated as follows:

Total Claims	27 - 20 =	7 x \$18 =	\$ 126.00
Independent Claims	2 - 3 =	0 x \$78 =	\$ 000.00
Base Filing Fee	(\$840.00)		\$ 840.00
Multiple Dep. Claim Fee	(\$260.00)		\$ 260.00
TOTAL FILING FEE			\$ 1226.00
Recordation of Assignment Fee			\$ 40.00
TOTAL U.S. GOVERNMENT FEE			\$ 1266.00

Checks for the statutory filing fee of \$ **1226.00** and Assignment recordation fee of \$ **40.00** are attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. 1.16 and 1.17 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Priority is claimed from:

Japanese Patent Application

005036/1997

005037/1997

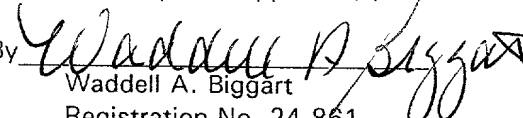
Filing Date

January 14, 1997

January 14, 1997

The Office is invited to contact the above firm on any question which might arise on the above-named application. Any contact that the Office might need to make should be directed to J. Frank Osha, Registration No. 24,625, at (202)293-7060.

Respectfully submitted,
SUGHRUE, MION, ZINN, MACPEAK & SEAS
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By 
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WAB:rtw

SPECIFICATION

PROCESS FOR THE PREPARATION OF CYCLOPENTADIENYL METAL SALT
AND PROCESS FOR THE PREPARATION OF DERIVATIVE OF
CYCLOPENTADIENE USING THE SAME

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Field of the Invention

The present invention relates to a process for the preparation of a cyclopentadienyl metal salt and a process for the preparation of a cyclopentadiene derivative using the same.

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Background Art

Cyclopentadienyl metal salts and derivatives of cyclopentadiene derived from such metal salts are important intermediates which are used in various fields such as the preparation of medicines, agrochemicals, metallocenes, etc. An effective process for the preparation of cyclopentadienyl metal salts comprises removing hydrogen atoms from cyclopentadiene with bases to synthesize corresponding metal salts, and for example, such a process using butyl lithium is known (J. Organomet. Chem., 462, 1993, 57-67).

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However, the process using butyl lithium has disadvantages such that (1) used reagents are expensive, (2) it requires low-temperature facilities to perform the reaction, and (3) the reaction should be carried out at the low concentration of reagents in an industrial scale, and thus the productivity decreases, since the desired product cannot effectively be obtained if the reaction is not carried out at a low temperature, although the amount of

reaction heat is large. As a matter of course, cyclopentadiene derivatives derived from cyclopentadienyl metal salts have the same problems.

Also, a process using an alkali metal hydride is known. However, this process has disadvantages such that (1) the kinds of substrates are extremely limited, (2) mineral oils, which are usually contained as a stabilizer in marketed alkali metal hydrides, should be beforehand removed, and thus the use of the alkali metal hydrides is unfavorable from the viewpoint of disaster measures, and the number of process steps in the industrial production.

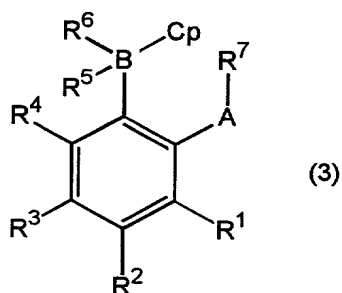
Disclosure of the Invention

In view of the above circumstances, the present inventors extensively studied a process which can easily produce a cyclopentadienyl metal salt without the use of expensive reagents and low-temperature facilities, and has no substrate specificity. As a result, it has been found that such an object can be accomplished by the reaction of a cyclopentadiene and a metal hydride in the presence of an amine compound, and thus the present invention has been completed.

Accordingly, the present invention provides

1. a process for the preparation of a cyclopentadienyl metal salt comprising the step of reacting a cyclopentadiene and a metal hydride in the presence of an amine compound, and

2. a process for the preparation of a cyclopentadiene derivative of the formula (3):



wherein

A is an atom of the 16 group of the Periodic Table,

B is an atom of the 14 group of the Periodic Table,

R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are the same or different and independently represent a hydrogen atom, a fluorine atom, a C_1 - C_{20} alkyl group which may optionally be substituted with a fluorine atom, a C_7 - C_{20} aralkyl group which may optionally be substituted with a fluorine atom, a C_6 - C_{20} aryl group which may optionally be substituted with a fluorine atom, a C_1 - C_{20} substituted silyl group, a C_1 - C_{20} alkoxyl group which may optionally be substituted with a fluorine atom, a C_7 - C_{20} aralkyloxyl group which may optionally be substituted with a fluorine atom, a C_6 - C_{20} aryloxyl group which may optionally be substituted with a fluorine atom, or a C_2 - C_{20} di-substituted amino group which may optionally be substituted with a fluorine atom, provided that any two or more of R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may together form a ring,

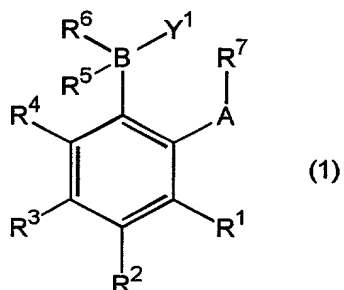
R^7 is a hydrocarbon group which may optionally be substituted with a fluorine atom, or a tri-substituted silyl group,

and

Cp is a cyclopentadiene ring comprising the step of reacting a halide compound of the

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formula (1):



wherein A, B, R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ are the same as defined above, and Y¹ is a chlorine atom, a bromine atom or an iodine atom

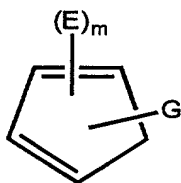
with a cyclopentadiene of the formula (2):



wherein Cp is the same as defined above, in the presence of a metal hydride and an amine compound.

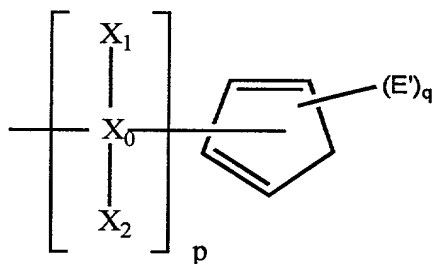
Here, the process according to the first aspect of the present invention, that is, the preparation process of a cyclopentadienyl metal salt by the reaction of a cyclopentadiene and a metal hydride in the presence of an amine compound, will be explained.

Cyclopentadienes used in the present invention may be any compounds having a cyclopentadienyl moiety. For example, a cyclopentadiene of the formula (2), which is used in the processes according to the first and second aspects of the present invention, may be a compound of the formula (2a):



wherein m is an integer of 0 to 5, E groups are the same or different and independently represent a C₁-C₈ alkyl group, a phenyl group, a naphthyl group, or a tri-substituted silyl group having substituents selected from the group consisting of a C₁-C₄ alkyl group and a phenyl group, provided that, when two E groups are present on adjacent carbon atoms, they may be bonded at their ends to form a benzene ring, a cyclohexane ring or a cyclohexene ring, which is condensed with the cyclopentadienyl ring,

G is a hydrogen atom when m is 5, or when m is 0 to 4, G is a hydrogen atom or a group of the formula (2b):



wherein p is an integer of 1 or 2, q is an integer of 0 to 4, X₀ is a carbon atom or a silicon atom, X₁ and X₂ are the same or different and independently represent a hydrogen atom, a C₁-C₄ alkyl group or a phenyl group, E' is a substituent selected from those defined for E, provided that when X₀ is a silicon atom, X₁ and X₂ are not hydrogen atoms.

Herein, the cyclopentadienyl group includes a mixture of its tautomers, which is usually obtained. The chemical structures in this specification represent a part of tautomers as typical examples.

Examples of cyclopentadienes, which are compounds having a cyclopentadienyl moiety, include

cyclopentadiene compounds such as cyclopentadiene, methylcyclopentadiene, dimethylcyclopentadiene, trimethylcyclopentadiene, tetramethylcyclopentadiene, pentamethylcyclopentadiene, ethylcyclopentadiene, n-propylcyclopentadiene, isopropylcyclopentadiene, n-butylcyclopentadiene, sec.-butylcyclopentadiene, tert.-butylcyclopentadiene, n-pentylcyclopentadiene, neopentylcyclopentadiene, n-hexylcyclopentadiene, n-octylcyclopentadiene, phenylcyclopentadiene, naphthylcyclopentadiene, trimethylsilylcyclopentadiene, triethylsilylcyclopentadiene, tert.-butyldimethylsilylcyclopentadiene, etc.;

indene compounds such as indene, methylindene, dimethylindene, ethylindene, n-propylindene, isopropylindene, n-butylindene, sec.-butylindene, tert.-butylindene, n-pentylindene, neopentylindene, n-hexylindene, n-octylindene, n-decylindene, phenylindene, methylphenylindene, naphthylindene, trimethylsilylindene, triethylsilylindene, tert.-butyldimethylsilylindene, tetrahydroindene, etc.;

fluorene compounds such as fluorene, methylfluorene, ethylfluorene, n-propylfluorene, isopropylfluorene, n-butylfluorene, sec.-butylfluorene, tert.-butylfluorene, n-pentylfluorene, neopentylfluorene, n-hexylfluorene, n-octylfluorene, n-decylfluorene, n-dodecylfluorene, phenylfluorene, naphthylfluorene, trimethylsilylfluorene, triethylsilylfluorene, tert.-butyldimethylsilylfluorene, etc.;

biscyclopentadiene compounds such as biscyclopentadienylmethane, biscyclopentadienylethane,

biscyclopentadienylpropane, biscyclopentadienylbutane,
 biscyclopentadienylpentane, biscyclopentadienylhexane,
 biscyclopentadienyldimethylsilane,
 biscyclopentadienyldiphenylsilane,
 5 bismethylcyclopentadienyldimethylsilane,
 bisdimethylcyclopentadienyldimethylsilane,
 bistrimethylcyclopentadienyldimethylsilane,
 bistetramethylcyclopentadienyldimethylsilane,
 biscyclopentadienyltetramethyldisilane, etc.;

10 bisindene compounds such as bisindenylmethane,
 bisindenylethane, bisindenylpropane, bisindenylbutane,
 bisindenylpentane, bisindenylhexane,
 bisindenyldimethylsilane, bisindenyldiphenylsilane,
 bismethylindenyl dimethylsilane,
 15 bisdimethylindenyl dimethylsilane,
 bisindenyltetramethyldisilane, etc.;

bisfluorene compounds such as bisfluorenylmethane,
 bisfluorenylethane, bisfluorenylpropane, bisfluorenylbutane,
 bisfluorenylpentane, bisfluorenylhexane,
 20 bisfluorenyldimethylsilane, bisfluorenyldiphenylsilane,
 bisfluorenyltetramethyldisilane, etc.;

complex compounds such as
 cyclopentadienylindenylmethane,
 cyclopentadienylindenylethane,
 25 cyclopentadienylindenylpropane,
 cyclopentadienylindenylbutane,
 cyclopentadienylindenylpentane,
 cyclopentadienylindenylhexane,
 cyclopentadienylindenyldimethylsilane,

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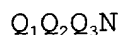
cyclopentadienylindenyl diphenylsilane,
 methylcyclopentadienylindenyl dimethylsilane,
 dimethylcyclopentadienylindenyl dimethylsilane,
 trimethylcyclopentadienylindenyl dimethylsilane,
 5 tetramethylcyclopentadienylindenyl dimethylsilane,
 cyclopentadienylindenyl tetramethyldisilane,
 cyclopentadienylfluorenylmethane,
 cyclopentadienylfluorenylethane,
 cyclopentadienylfluorenylpropane,
 10 cyclopentadienylfluorenylbutane,
 cyclopentadienylfluorenylpentane,
 cyclopentadienylfluorenylhexane,
 cyclopentadienylfluorenyl dimethylsilane,
 cyclopentadienylfluorenyl diphenylsilane,
 15 methylcyclopentadienylfluorenyl dimethylsilane,
 dimethylcyclopentadienylfluorenyl dimethylsilane,
 trimethylcyclopentadienylfluorenyl dimethylsilane,
 tetramethylcyclopentadienylfluorenyl dimethylsilane,
 cyclopentadienylfluorenyl tetramethyldisilane, etc.

20 The process of the present invention can easily
 produce desired compounds at a high yield, when
 cyclopentadiene compounds having two or more substituents
 are used.

Examples of metal hydrides include alkali metal
 25 hydrides such as lithium hydride, sodium hydride, potassium
 hydride, etc.; and alkaline earth metal hydrides such as
 calcium hydride, etc. The amount of a metal hydride is
 usually from 0.5 to 3 moles, preferably from 0.9 to 2.0
 moles, per one mole of the compound (2). Sodium hydride

and potassium hydride can be used in the form of a marketed product containing mineral oils, although they may be used after washing the mineral oils off with hydrocarbon solvents such as hexane, etc.

As an amine compound, a compound of the following formula (4) is exemplified:



wherein Q_1 , Q_2 and Q_3 are the same or different and independently represent a hydrogen atom, a C_1 - C_8 alkyl group, or a C_3 - C_8 cycloalkyl group; or a phenyl group, a naphthyl group, a benzyl group, a naphthylmethyl group or a pyridyl group, which may optionally be substituted with at least one substituent selected from the group consisting of a halogen atom, a C_1 - C_4 alkyl group, a C_1 - C_4 alkoxy group, a carboxyl group, a C_1 - C_4 alkoxy carbonyl group, a nitro group, an amino group, a phenyl group, a naphthyl group and a benzyl group; or the terminals of Q_1 and Q_2 are bonded each other to form a C_4 - C_5 alkylene group which may optionally be substituted with at least one C_1 - C_3 alkyl group, or a group of the formula: $(-CH_2CH_2)_2-O$ or $(-CH_2CH_2)_2N-Q_4$ in which Q_4 is a substituent selected from those defined for Q_3 , or Q_3 may be an ethylene group or a group of the formula: $-(CH_2)_3N=$ and bonded to a ring formed by Q_2 and Q_3 , provided that Q_1 , Q_2 and Q_3 are not hydrogen atoms at the same time.

Specific examples of amine compounds are

primary amines including primary amines, for example, primary amines such as aniline, chloroaniline, bromoaniline, fluoroaniline, dichloroaniline, dibromoaniline,

difluoroaniline, trichloroaniline, tribromoaniline,
 trifluoroaniline, tetrachloroaniline, tetrabromoaniline,
 tetrafluoroaniline, pentachloroaniline, pentafluoroaniline,
 nitroaniline, dinitroaniline, hydroxyaniline,
 5 phenylenediamine, anisidine, dimethoxyaniline,
 trimethoxyaniline, ethoxyaniline, diethoxyaniline,
 triethoxyaniline, n-propoxyaniline, isopropoxyaniline, n-
 butoxyaniline, sec.-butoxyaniline, isobutoxyaniline, tert.-
 butoxyaniline, phenoxyaniline, methylaniline, ethylaniline,
 10 n-propylaniline, isopropylaniline, n-butylaniline, sec.-
 butylaniline, isobutylaniline, tert.-butylaniline,
 dimethylaniline, diethylaniline, di-n-propylaniline,
 diisopropylaniline, di-n-butylaniline, di-sec.-butylaniline,
 diisobutylaniline, di-tert.-butylaniline, trimethylaniline,
 15 triethylaniline, diisopropylaniline, phenylaniline,
 benzylianiline, aminobenzoic acid, methyl aminobenzoate,
 ethyl aminobenzoate, n-propyl aminobenzoate, isopropyl
 aminobenzoate, n-butyl aminobenzoate, isobutyl
 aminobenzoate, sec.-butyl aminobenzoate, tert.-butyl
 20 aminobenzoate, etc.; as well as naphthylamine,
 naphthylmethylaniline, benzylamine, propylamine, butylamine,
 pentylamine, hexylamine, cyclohexylamine, heptylamine,
 octylamine, 2-aminopyridine, 3-aminopyridine, 4-
 aminopyridine, etc.,
 25 secondary amines such as N-methylaniline, N-
 ethylaniline, diphenylamine, N-methylchloroaniline, N-
 methylbromoaniline, N-methylfluoroaniline, N-
 methylanisidine, N-methylmethylaniline, N-
 methylethylaniline, N-methyl-n-propylaniline, N-

methyllisopropylaniline, diethylamine, diproylamine,
 diisopropylamine, dipentylamine, dihexylamine,
 dicyclohexylamine, diheptylamine, dioctylamine, morpholine,
 piperidine, 2,2,6,6-tetramethylpiperidine, pyrrolidine, 2-
 5 methylaminopyridine, 3-methylaminopyridine, 4-
 methylaminopyridine, etc.,

tertiary amines such as N,N-dimethylaniline, N,N-
 dimethylchloroaniline, N,N-dimethylbromoaniline, N,N-
 dimethylfluoroaniline, N,N-dimethylanisidine, N-
 10 methylmethylaniline, N,N-dimethylethylaniline, N,N-
 dimethyl-n-propylaniline, N,N-dimethylisopropylaniline, 2-
 dimethylaminopyridine, 3-dimethylaminopyridine, 4-
 dimethylaminopyridine, 1,4-diazabicyclo[2.2.2]octane, 1,5-
 diazabicyclo[4.3.0]non-5-ene, 1,8-diazabicyclo[5.4.0]undec-
 15 7-ene, etc.

Among them, primary and secondary amines are
 preferably used. More preferably, primary anilines are
 used.

The amount of an amine compound is usually from 0.001
 20 to 2 moles, preferably from 0.01 to 0.5 mole, per one mole
 of a metal hydride.

The reaction is usually carried out in a solvent which
 is inactive to the reaction. Examples of solvents are
 aprotic solvents, for example, aromatic hydrocarbon
 25 solvents such as benzene, toluene, xylene, etc.; aliphatic
 hydrocarbon solvents such as pentane, hexane, heptane,
 octane cyclohexane, etc.; ether solvents such as diethyl
 ether, methyl tert.-butyl ether, tetrahydrofuran, 1,4-
 dioxane, etc.; amide solvents such as hexamethylphosphoric

amide, dimethylformamide, dimethylacetamide, N-methylpyrrolidone, etc.; halogen-containing solvents such as chlorobenzene, dichlorobenzene, etc. These solvents may be used singly or in admixture of two or more solvents.

5 The amount of a solvent is usually from 1 to 200 wt. parts, preferably from 3 to 30 wt. parts, per 1 wt. part of a cyclopentadiene.

10 To carry out the reaction, a cyclopentadiene, a metal hydride and an amine compound are mixed at the same time in a solvent, or a metal hydride and an amine compound are firstly mixed, and then a cyclopentadiene is added to the mixture.

15 A reaction temperature is not limited, but is preferably in a range in which no low-temperature facilities are necessary, for the industrial production. For example, a reaction temperature is usually in the range between 0 and 70°C, preferably between 10 and 60°C.

20 The above reaction effectively provides a desired cyclopentadienyl metal salt. The obtained cyclopentadienyl metal salt may be used in the form of a reaction mixture, or may be isolated from the reaction mixture. In general, the reaction mixture as such can satisfactorily be used.

25 Now, the process according to the second aspect of the present invention, that is, the preparation process of a cyclopentadiene derivative of the formula (3) by the reaction of a halide compound of the formula (1) and a cyclopentadiene of the formula (2) in the presence of a metal haride and an amine compound will be explained.

Examples of an atom of the 16 group of the Periodic

Table, which is represented by "A" in the formula (1), include an oxygen atom, a sulfur atom, a selenium atom, etc. An oxygen atom and a sulfur atom are preferable, and an oxygen atom is more preferable.

5 Examples of an atom of the 14 group of the Periodic Table, which is represented by "B", include a carbon atom, a silicon atom, a germanium atom, etc. A carbon atom and a silicon atom are preferable.

10 Examples of a C_1 - C_{20} alkyl group for R^1 , R^2 , R^3 , R^4 , R^5 or R^6 include a methyl group, an ethyl group, a n-propyl group, an isopropyl group, a n-butyl group, a sec.-butyl group, a tert.-butyl group, a n-pentyl group, a neopentyl group, an amyl group, a n-hexyl group, a n-octyl group, a n-decyl group, a n-dodecyl group, a n-pentadecyl group, a
15 n-eicosyl group, etc. Among them, a methyl group, an ethyl group, an isopropyl group, a tert.-butyl group and an amyl group are preferable.

 Any one of these alkyl groups may optionally be substituted with one or more fluorine atoms. Examples of a
20 fluorinated C_1 - C_{20} alkyl group include a fluoromethyl group, a difluoromethyl group, a trifluoromethyl group, a fluoroethyl group, a difluoroethyl group, a trifluoroethyl group, a tetrafluoroethyl group, a pentafluoroethyl group, a perfluoropropyl group, a perfluorobutyl group, a
25 perfluoropentyl group, a perfluorohexyl group, a perfluorooctyl group, a perfluorododecyl group, a perfluoropentadecyl group, a perfluoroeicosyl group, etc.

 Examples of a C_7 - C_{20} aralkyl group for R^1 , R^2 , R^3 , R^4 , R^5 or R^6 include a benzyl group, a (2-methylphenyl)methyl

group, a (3-methylphenyl)methyl group, a (4-methylphenyl)methyl group, a (2,3-dimethylphenyl)methyl group, a (2,4-dimethylphenyl)methyl group, a (2,5-dimethylphenyl)methyl group, a (2,6-dimethylphenyl)methyl group, a (3,4-dimethylphenyl)methyl group, a (4,6-dimethylphenyl)methyl group, a (2,3,4-trimethylphenyl)-methyl group, a (2,3,5-trimethylphenyl)methyl group, a (2,3,6-trimethylphenyl)methyl group, a (3,4,5-trimethylphenyl)methyl group, a (2,4,6-trimethylphenyl)-methyl group, a (2,3,4,5-tetramethylphenyl)methyl group, a (2,3,4,6-tetramethylphenyl)methyl group, a (2,3,5,6-tetramethylphenyl)methyl group, a (pentamethylphenyl)-methyl group, an (ethylphenyl)methyl group, a (n-propylphenyl)methyl group, an (isopropylphenyl)methyl group, a (n-butylphenyl)methyl group, a (sec.-butylphenyl)methyl group, a (tert.-butylphenyl)methyl group, a (n-pentylphenyl)methyl group, a (neopentylphenyl)methyl group, a (n-hexylphenyl)methyl group, a (n-octylphenyl)methyl group, a (n-decylphenyl)methyl group, a (n-tetradecylphenyl)methyl group, a naphthylmethyl group, an anthracenylmethyl group, etc. Among them, a benzyl group is preferable. Any one of these aralkyl groups may optionally be substituted by one or more fluorine atoms.

Examples of a C₆-C₂₀ aryl group for R¹, R², R³, R⁴, R⁵ or R⁶ include a phenyl group, a 2-tolyl group, a 3-tolyl group, a 4-tolyl group, a 2,3-xylyl group, a 2,4-xylyl group, a 2,5-xylyl group, a 2,6-xylyl group, a 3,4-xylyl group, a 3,5-xylyl group, a 2,3,4-trimethylphenyl group, a 2,3,5-trimethylphenyl group, a 2,3,6-trimethylphenyl group,

a 2,4,6-trimethylphenyl group, a 3,4,5-trimethylphenyl group, a 2,3,4,5-tetramethylphenyl group, a 2,3,4,6-tetramethylphenyl group, a 2,3,5,6-tetramethylphenyl group, a pentamethylphenyl group, an ethylphenyl group, a n-propylphenyl group, a isopropylphenyl group, a n-butylphenyl group, a sec.-butylphenyl group, a tert.-butylphenyl group, a n-pentylphenyl group, a neopentylphenyl group, a n-hexylphenyl group, a n-octylphenyl group, a n-decylphenyl group, a n-dodecylphenyl group, a tetradecylphenyl group, a naphthyl group, an anthracenyl group, etc. Among them, a phenyl group is preferable. Any one of these aryl groups may optionally be substituted by one or more fluorine atoms.

A substituted silyl group for R^1 , R^2 , R^3 , R^4 , R^5 or R^6 means a silyl group which is substituted by one or more hydrocarbon groups. Here, examples of hydrocarbon groups include C_1 - C_{10} hydrocarbon groups such as a methyl group, an ethyl group, a n-propyl group, an isopropyl group, a n-butyl group, a sec.-butyl group, a tert.-butyl group, an isobutyl group, a n-pentyl group, a n-hexyl group, a cyclohexyl group, etc.; aryl groups such as a phenyl group, etc. Examples of a C_1 - C_{20} substituted silyl group include mono-substituted silyl groups having 1 to 20 carbon atoms such as a methylsilyl group, an ethylsilyl group, a phenylsilyl group, etc.; di-substituted silyl groups having 2 to 20 carbon atoms such as a dimethylsilyl group, a diethylsilyl group, a diphenylsilyl group, etc.; tri-substituted silyl groups having 3 to 20 carbon atoms such as a trimethylsilyl group, a triethylsilyl group, a tri-n-

propylsilyl group, a triisopropylsilyl group, a tri-n-butylsilyl group, a tri-sec.-butylsilyl group, a tri-tert.-butylsilyl group, a triisobutylsilyl group, a tert.-butyldimethylsilyl group, a tri-n-pentylsilyl group, a tri-n-hexylsilyl group, a tricyclohexylsilyl group, a triphenylsilyl group, etc. Among them, a trimethylsilyl group, a tert.-butyldimethylsilyl group and a triphenylsilyl group are preferable. Any one of the hydrocarbon groups of these substituted silyl groups may optionally be substituted by one or more fluorine atoms.

Examples of a C_1 - C_{20} alkoxyl group for R^1 , R^2 , R^3 , R^4 , R^5 or R^6 include a methoxy group, an ethoxy group, a n-propoxy group, an isopropoxy group, a n-butoxy group, a sec.-butoxy group, a tert.-butoxy group, a n-pentyloxy group, a neopentyloxy group, a n-hexyloxy group, a n-octyloxy group, a n-dodecyloxy group, a n-pentadecyloxy group, a n-eicocyloxy group, etc. Among them, a methoxy group, an ethoxy group and a tert.-butoxy group are preferable. Any one of these alkoxyl groups may optionally be substituted by one or more fluorine atoms.

Examples of a C_7 - C_{20} aralkyloxy group for R^1 , R^2 , R^3 , R^4 , R^5 or R^6 include a benzyloxy group, a (2-methylphenyl)methoxy group, a (3-methylphenyl)methoxy group, a (4-methylphenyl)methoxy group, a (2,3-dimethylphenyl)methoxy group, a (2,4-dimethylphenyl)methoxy group, a (2,5-dimethylphenyl)methoxy group, a (2,6-dimethylphenyl)methoxy group, a (3,4-dimethylphenyl)methoxy group, a (3,5-dimethylphenyl)methoxy group, a (2,3,4-trimethylphenyl)methoxy group, a (2,3,5-

trimethylphenyl)methoxy group, a (2,3,6-
 trimethylphenyl)methoxy group, a (2,4,5-
 trimethylphenyl)methoxy group, a (2,4,6-
 trimethylphenyl)methoxy group, a (3,4,5-
 5 trimethylphenyl)methoxy group, a (2,3,4,5-
 tetramethylphenyl)methoxy group, a (2,3,4,6-
 tetramethylphenyl)methoxy group, a (2,3,5,6-
 tetramethylphenyl)methoxy group, a
 (pentamethylphenyl)methoxy group, an (ethylphenyl)methoxy
 10 group, a (n-propylphenyl)methoxy group, an
 (isopropylphenyl)methoxy group, a (n-butylphenyl)methoxy
 group, a (sec.-butylphenyl)methoxy group, a (tert.-
 butylphenyl)methoxy group, a (n-hexylphenyl)methoxy group,
 a (n-octylphenyl)methoxy group, a (n-decylphenyl)methoxy
 15 group, a (n-tetradecylphenyl)methoxy group, a
 naphthylmethoxy group, an anthracenylmethoxy group, etc.
 Among them a benzyloxy group is preferable. Any one of
 these aralkyloxyl groups may optionally be substituted by
 one or more fluorine atoms.

20 Examples of an aryloxyl group for R^1 , R^2 , R^3 , R^4 , R^5 or
 R^6 include C_6 - C_{20} aryloxyl groups such as a phenoxy group, a
 2-methylphenoxy group, a 3-methylphenoxy group, a 4-
 methylphenoxy group, a 2,3-dimethylphenoxy group, a 2,4-
 dimethylphenoxy group, a 2,5-dimethylphenoxy group, a 2,6-
 25 dimethylphenoxy group, a 3,4-dimethylphenoxy group, a 3,5-
 dimethylphenoxy group, a 2,3,4-trimethylphenoxy group, a
 2,3,5-trimethylphenoxy group, a 2,3,6-trimethylphenoxy
 group, a 2,4,5-trimethylphenoxy group, a 2,4,6-
 trimethylphenoxy group, a 3,4,5-trimethylphenoxy group, a

2,3,4,5-tetramethylphenoxy group, a 2,3,4,6-tetramethylphenoxy group, a 2,3,5,6-tetramethylphenoxy group, a pentamethylphenoxy group, an ethylphenoxy group, a n-propylphenoxy group, an isopropylphenoxy group, a n-butylphenoxy group, a sec.-butylphenoxy group, a tert.-butylphenoxy group, a n-hexylphenoxy group, a n-octylphenoxy group, a n-decylphenoxy group, a n-tetradecylphenoxy group, a naphthoxy group, an anthracenyloxy group, etc. Any one of these aryloxyl groups may optionally be substituted by one or more fluorine atoms.

A C_2-C_{20} disubstituted amino group for R^1 , R^2 , R^3 , R^4 , R^5 or R^6 means an amino group which is substituted by two hydrocarbon groups. Here, examples of hydrocarbon groups include C_2-C_{20} hydrocarbon groups such as a methyl group, an ethyl group, a n-propyl group, an isopropyl group, a n-butyl group, a sec.-butyl group, a tert.-butyl group, an isobutyl group, a n-pentyl group, a n-hexyl group, a cyclohexyl group, etc.; aryl groups such as a phenyl group, etc. Examples of the C_1-C_{10} disubstituted amino group include a dimethylamino group, a diethylamino group, a di-n-propylamino group, a diisopropylamino group, a di-n-butylamino group, a di-sec.-butylamino group, a di-tert.-butylamino group, a diisobutylamino group, a tert.-butylisopropylamino group, a di-n-hexylamino group, a di-n-octylamino group, a di-n-decylamino group, a diphenylamino group, a bistrimethylsilylamino group, a bis-tert.-butyldimethylsilylamino group, etc. Among them, a dimethylamino group and a diethylamino group are preferable.

Any one of these disubstituted amino groups may optionally be substituted by one or more fluorine atoms.

Any two or more groups of R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may optionally bond each other to form a ring or rings.

5 Examples of a hydrocarbon group for R^7 include C_1 - C_{10} alkyl groups such as a methyl group, an ethyl group, a propyl group, a hexyl group, a decyl group, etc.; C_2 - C_{10} alkenyl groups such as a vinyl group, an allyl group, a propenyl group, a 2-methyl-2-propenyl group, a homoallyl
10 group, a hexenyl group, a decenyl group, etc.; alkoxyalkyl groups such as a methoxymethyl group, a methoxyethoxymethyl group, etc.; C_7 - C_{12} aralkyl groups such as a benzyl group, a (4-methylphenyl)methyl group, a (2,4,6-trimethylphenyl)-methyl group, etc. Any one of these hydrocarbon groups may
15 optionally be substituted by one or more halogen atoms. Examples of halogen-substituted hydrocarbon groups include a 2-chloro-2-propenyl group, and the like.

 Examples of a tri-substituted silyl group include a trimethylsilyl group, a triethylsilyl group, a tri-n-
20 propylsilyl group, a triisopropylsilyl group, a tri-n-butylsilyl group, a tri-sec.-butylsilyl group, a tri-tert.-butylsilyl group, a triisobutylsilyl group, a tert.-butyldimethylsilyl group, a tri-n-pentylsilyl group, a tri-n-hexylsilyl group, a tricyclohexylsilyl group, a
25 triphenylsilyl group, etc.

 Specific examples of the compound (1) in which B is a carbon atom include 2-bromo-2-(2-methoxyphenyl)propane, 2-bromo-2-(2-methoxy-3-methylphenyl)propane, 2-bromo-2-(2-methoxy-3,5-dimethylphenyl)propane, 2-bromo-2-(3-tert.-

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butyl-2-methoxyphenyl)propane, 2-bromo-2-(3-tert.-butyl-2-methoxy-5-methylphenyl)propane, 2-bromo-2-(3,5-di-tert.-butyl-2-methoxyphenyl)propane, 2-bromo-2-(2-methoxy-3-phenylphenyl)propane, 2-bromo-2-(2-methoxy-5-methyl-3-phenylphenyl)propane, 2-bromo-2-(3-tert.-butyldimethylsilyl-2-methoxyphenyl)propane, 2-bromo-2-(3-tert.-butyldimethylsilyl-2-methoxy-5-methylphenyl)propane, 2-bromo-2-(2-methoxy-3-trimethylsilylphenyl)propane, 2-bromo-2-(2-methoxy-5-methyl-3-trimethylsilylphenyl)propane, 2-bromo-2-(3,5-diamyl-2-methoxyphenyl)propane, 2-bromo-2-(3-tert.-butyl-2,5-dimethoxyphenyl)propane, 2-bromo-2-(3-tert.-butyl-5-chloro-2-methoxyphenyl)propane, 2-bromo-2-(2-allyloxyphenyl)propane, 2-bromo-2-(2-allyloxy-3-methylphenyl)propane, 2-bromo-2-(2-allyloxy-3,5-dimethylphenyl)propane, 2-bromo-2-(2-allyloxy-3-tert.-butylphenyl)propane, 2-bromo-2-(2-allyloxy-3-tert.-butyl-5-methylphenyl)propane, 2-bromo-2-(2-allyloxy-3,5-di-tert.-butylphenyl)propane, 2-bromo-2-(2-allyloxy-3-phenylphenyl)propane, 2-bromo-2-(2-allyloxy-5-methyl-3-phenylphenyl)propane, 2-bromo-2-(2-allyloxy-3-tert.-butyldimethylsilylphenyl)propane, 2-bromo-2-(2-allyloxy-3-tert.-butyldimethylsilyl-4-methylphenyl)propane, 2-bromo-2-(2-allyloxy-3-trimethylsilylphenyl)propane, 2-bromo-2-(2-allyloxy-5-methyl-3-trimethylsilylphenyl)propane, 2-bromo-2-(2-allyloxy-3,5-diamylphenyl)propane, 2-bromo-2-(2-allyloxy-3-tert.-butyl-5-methoxyphenyl)propane, 2-bromo-2-(2-allyloxy-3-tert.-butyl-5-chlorophenyl)propane, 2-bromo-2-(1-allyloxynaphthalen-2-yl)propane, etc.

Examples of the compound (1) in which B is a carbon

atom also include analogous compounds to the above exemplified compounds in which a methoxy or allyloxy group is replaced by a benzyloxy group, an ethoxy group, a trimethylsilyloxy group, a tert.-butyldimethylsilyloxy group or a methoxymethoxy group; or propane is replaced by methane, ethane, butane, pentane, hexane, phenylmethane or diphenylmethane; or a bromo moiety is replaced by an iodo moiety.

Examples of the compound (1) in which B is a silicon atom include chloro(2-methoxyphenyl)dimethylsilane, chloro(2-methoxy-3-methylphenyl)dimethylsilane, chloro(2-methoxy-3,5-dimethylphenyl)dimethylsilane, (3-tert.-butyl-2-methoxyphenyl)chlorodimethylsilane, (3-tert.-butyl-2-methoxy-5-methylphenyl)chlorodimethylsilane, (3,5-di-tert.-butyl-2-methoxyphenyl)chlorodimethylsilane, chloro(2-methoxy-3-phenylphenyl)dimethylsilane, chloro(2-methoxy-5-methyl-3-phenylphenyl)dimethylsilane, (3-tert.-butyldimethylsilyl-2-methoxyphenyl)chlorodimethylsilane, (3-tert.-butyldimethylsilyl-2-methoxy-5-methylphenyl)chlorodimethylsilane, chloro(2-methoxy-3-trimethylsilylphenyl)dimethylsilane, chloro(2-methoxy-5-methyl-3-trimethylsilylphenyl)dimethylsilane, (3,5-diamyl-2-methoxyphenyl)chlorodimethylsilane, (3-tert.-butyl-2,5-dimethoxyphenyl)chlorodimethylsilane, (3-tert.-butyl-5-chloro-2-methoxyphenyl)chlorodimethylsilane, (2-allyloxyphenyl)chlorodimethylsilane, (2-allyloxy-3-methylphenyl)chlorodimethylsilane, (2-allyloxy-3,5-dimethylphenyl)chlorodimethylsilane, (2-allyloxy-3-tert.-butylphenyl)chlorodimethylsilane, (2-allyloxy-3-tert.-

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butyl-5-methylphenyl)chlorodimethylsilane, (2-allyloxy-3,5-di-tert.-butylphenyl)chlorodimethylsilane, (2-allyloxy-3-phenylphenyl)chlorodimethylsilane, (2-allyloxy-5-methyl-3-phenylphenyl)chlorodimethylsilane, (2-allyloxy-3-tert.-butyldimethylsilylphenyl)chlorodimethylsilane, (2-allyloxy-3-tert.-butyldimethylsilyl-4-methylphenyl)chlorodimethylsilane, (2-allyloxy-3-trimethylsilylphenyl)chlorodimethylsilane, (2-allyloxy-5-methyl-3-trimethylsilylphenyl)chlorodimethylsilane, (2-allyloxy-3,5-diamylphenyl)chlorodimethylsilane, (2-allyloxy-3-tert.-butyl-5-methoxyphenyl)chlorodimethylsilane, (2-allyloxy-3-tert.-butyl-5-chlorophenyl)chlorodimethylsilane, (1-allyloxynaphthalen-2-yl)chlorodimethylsilane, etc.

Examples of the compound (1) in which B is a silicon atom also include analogous compounds to the above exemplified compounds in which a methoxy group or an allyloxy group is replaced by a benzyloxy group, an ethoxy group, a trimethylsilyloxy group, a tert.-butyldimethylsilyloxy group or a methoxymethoxy group; or a chlorodimethylsilane group is replaced by a chlorodiethylsilane group, a chlorodiphenylsilane group, chlorodimethoxysilane group, a bromodimethylsilane group or a dimethyliodosilane group.

The compound (2) may be any compound having a cyclopentadienyl moiety. Examples of the compound (2) may be the same as those exemplified for the compound (2a).

Examples of an amine compound may be the same as those used in the process according to the first aspect of the

present invention.

The reaction is usually carried out in a solvent which is inactive to the reaction. Examples of such solvents are aprotic solvents, for example, aromatic hydrocarbon solvents such as benzene, toluene, xylene, etc.; aliphatic hydrocarbon solvents such as pentane, hexane, heptane, octane, cyclohexane, etc.; ether solvents such as diethyl ether, methyl tert.-butyl ether, tetrahydrofuran, 1,4-dioxane, etc.; amide solvents such as hexamethylphosphoric amide, dimethylformamide, dimethylacetamide, N-methylpyrrolidone, etc.; halogen-containing solvents such as chlorobenzene, dichlorobenzene, etc. These solvents may be used singly or in admixture of two or more solvents. The amount of a solvent is usually from 1 to 200 wt. parts, preferably from 3 to 30 wt. parts, per 1 wt. part of a cyclopentadiene.

This reaction is usually carried out by mixing a metal hydride, an amine compound and the compound (2) in a solvent, and then adding the compound (1), although the desired compound (3) can be synthesized by mixing all the compounds at the same time.

A reaction temperature is not limited, but is preferably in a range in which no low-temperature facilities are necessary, for the industrial production. For example, a reaction temperature is usually in the range between 0 and 70°C, preferably between 10 and 60°C.

The amount of the compound (2) is usually in the range between 0.5 and 5 moles, preferably between 0.8 and 3 moles, per one mole of the compound (1).

Examples of metal hydrides include alkali metal hydrides such as lithium hydride, sodium hydride, potassium hydride, etc.; and alkaline earth metal hydrides such as calcium hydride, etc. The amount of a metal hydride is usually from 0.5 to 3 moles, preferably from 0.9 to 2.0 moles, per one mole of the compound (2). Sodium hydride and potassium hydride can be used in the form of a marketed product containing mineral oils, although they may be used after washing the mineral oils off with hydrocarbon solvents such as hexane, etc.

The amount of an amine compound is usually from 0.001 to 2 moles, preferably from 0.01 to 0.5 mole, per one mole of a metal hydride.

After the completion of the reaction, water, or an acidic aqueous solution such as the aqueous solution of ammonium chloride or hydrochloric acid is added to the reaction mixture. Then, the mixture was separated to an organic phase and an aqueous phase, and the solution of the compound (3) is recovered in the form of the organic phase.

When a solvent miscible with water is used in the reaction or when a reaction mixture cannot be separated to an organic phase and an aqueous phase since the amount of a solvent used in the reaction is low, an organic solvent, which is insoluble in water such as toluene, ethyl acetate, chlorobenzene and the like, can be added to the reaction mixture, and then the reaction mixture is separated to an organic phase and an aqueous phase.

The compound (3) can be isolated from the organic phase by concentration. If desired, the compound (3) can

be purified by distillation, column chromatography, etc.

In the obtained compound (3), examples of a group having a cyclopentadiene moiety, which is represented by Cp, may be the groups exemplified for the compound (2a). In

particular, examples of such a group include a η^5 -cyclopentadienyl group, a η^5 -methylcyclopentadienyl group, a η^5 -dimethylcyclopentadienyl group, a η^5 -trimethylcyclopentadienyl group, a η^5 -tetramethylcyclopentadienyl group, a η^5 -ethylcyclopentadienyl group, a η^5 -n-propylcyclopentadienyl group, a η^5 -isopropylcyclopentadienyl group, a η^5 -n-butylcyclopentadienyl group, a η^5 -sec.-butylcyclopentadienyl group, a η^5 -tert.-butylcyclopentadienyl group, a η^5 -n-pentylcyclopentadienyl group, a η^5 -neopentylcyclopentadienyl group, a η^5 -n-hexylcyclopentadienyl group, a η^5 -n-octylcyclopentadienyl group, a η^5 -phenylcyclopentadienyl group, a η^5 -naphthylcyclopentadienyl group, a η^5 -trimethylsilylcyclopentadienyl group, a η^5 -triethylsilylcyclopentadienyl group, a η^5 -tert.-butyldimethylsilylcyclopentadienyl group, a η^5 -indenyl group, a η^5 -methylindenyl group, a η^5 -dimethylindenyl group, a η^5 -ethylindenyl group, a η^5 -n-propylindenyl group, a η^5 -isopropylindenyl group, a η^5 -n-butylindenyl group, a η^5 -sec.-butylindenyl group, a η^5 -tert.-butylindenyl group, a η^5 -n-pentylindenyl group, a η^5 -neopentylindenyl group, a η^5 -n-hexylindenyl group, a η^5 -n-octylindenyl group, a η^5 -n-decylindenyl group, a η^5 -phenylindenyl group, a η^5 -methylphenylindenyl group, a η^5 -naphthylindenyl group, a

η^5 -trimethylsilylindenyl group, a η^5 -triethylsilylindenyl group, a η^5 -tert.-butyldimethylsilylindenyl group, a η^5 -tetrahydroindenyl group, a η^5 -fluorenyl group, a η^5 -methylfluorenyl group, a η^5 -dimethylfluorenyl group, a η^5 -ethylfluorenyl group, a η^5 -diethylfluorenyl group, a η^5 -n-propylfluorenyl group, a η^5 -di-n-propylfluorenyl group, a η^5 -isopropylfluorenyl group, a η^5 -diisopropylfluorenyl group, a η^5 -n-butylfluorenyl group, a η^5 -sec.-butylfluorenyl group, a η^5 -tert.-butylfluorenyl group, a η^5 -di-n-butylfluorenyl group, a η^5 -di-sec.-butylfluorenyl group, a η^5 -di-tert.-butylfluorenyl group, a η^5 -n-pentylfluorenyl group, a η^5 -neopentylfluorenyl group, a η^5 -n-hexylfluorenyl group, a η^5 -n-octylfluorenyl group, a η^5 -n-decylfluorenyl group, a η^5 -n-dodecylfluorenyl group, a η^5 -phenylfluorenyl group, a η^5 -diphenylfluorenyl group, a η^5 -methylphenylfluorenyl group, a η^5 -naphthylfluorenyl group, a η^5 -trimethylsilylfluorenyl group, a η^5 -bis-trimethylsilylfluorenyl group, a η^5 -triethylsilylfluorenyl group, a η^5 -tert.-butyldimethylsilylfluorenyl group, etc.

Specific examples of the cyclopentadiene derivative (3) include 2-[(cyclopenta-1,4-dienyl)methyl]-1-methoxybenzene, 2-[(cyclopenta-1,4-dienyl)methyl]-1-methoxy-4,6-dimethylbenzene, 2-tert.-butyl-6-[(cyclopenta-1,4-dienyl)methyl]-1-methoxy-4-methylbenzene, 6-[(cyclopenta-1,4-dienyl)methyl]-1-methoxy-2-phenylbenzene, 1-tert.-butyldimethylsilyl-3-[(cyclopenta-1,4-dienyl)methyl]-2-methoxy-5-methylbenzene, 3-[(cyclopenta-1,4-dienyl)methyl]-2-methoxy-5-methyl-1-trimethylsilylbenzene, 2-tert.-butyl-6-[(cyclopenta-1,4-

- dienyl)methyl]-1,4-dimethoxybenzene, 3-tert.-butyl-1-chloro-5-[(cyclopenta-1,4-dienyl)methyl]-4-methoxybenzene, 2-tert.-butyl-6-[(cyclopenta-1,4-dienyl)methyl]-1-methoxybenzene, 2-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]-1-methoxybenzene, 2-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]-1-methoxy-4,6-dimethylbenzene, 6-tert.-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]-1-methoxy-4-methylbenzene, 6-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]-1-methoxy-2-phenylbenzene, 1-tert.-butyldimethylsilyl-3-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]-2-methoxy-5-methylbenzene, 3-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]-2-methoxy-5-methyl-1-trimethylsilylbenzene, 6-tert.-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]-1,4-dimethoxybenzene, 5-tert.-butyl-1-chloro-3-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]-4-methoxybenzene, 6-tert.-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]-1-methoxybenzene, 1-methoxy-2-[1-(4-methylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-methoxy-4,6-dimethyl-2-[1-(4-methylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 6-tert.-butyl-1-methoxy-4-methyl-2-[1-(4-methylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-methoxy-6-[1-(4-methylcyclopenta-1,4-dienyl)-1-methylethyl]-2-phenylbenzene, 1-tert.-butyldimethylsilyl-2-methoxy-5-methyl-3-[1-(4-methylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 2-methoxy-5-methyl-3-[1-(4-methylcyclopenta-1,4-dienyl)-1-methylethyl]-1-trimethylsilylbenzene, 6-tert.-butyl-1,4-dimethoxy-2-[1-(4-methylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 5-tert.-butyl-1-chloro-4-methoxy-3-[1-

- (4-methylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 6-tert.-butyl-1-methoxy-2-[1-(4-methylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 2-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]-1-methoxybenzene, 2-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]-1-methoxy-4,6-dimethylbenzene, 6-tert.-butyl-2-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]-1-methoxy-4-methylbenzene, 6-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]-1-methoxy-2-phenylbenzene, 1-tert.-butyldimethylsilyl-3-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]-2-methoxy-5-methylbenzene, 3-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]-2-methoxy-5-methyl-1-trimethylsilylbenzene, 6-tert.-butyl-2-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]-1,4-dimethoxybenzene, 5-tert.-butyl-1-chloro-3-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]-4-methoxybenzene, 6-tert.-butyl-2-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]-1-methoxybenzene, 1-methoxy-2-[1-(2,3,4,5-tetramethylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-methoxy-4,6-dimethyl-2-[1-(2,3,4,5-tetramethylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 6-tert.-butyl-1-methoxy-4-methyl-2-[1-(2,3,4,5-tetramethylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-methoxy-2-phenyl-6-[1-(2,3,4,5-tetramethylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-tert.-butyldimethylsilyl-2-methoxy-5-methyl-3-[1-(2,3,4,5-tetramethylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 2-methoxy-5-methyl-3-[1-(2,3,4,5-tetramethylcyclopenta-1,4-dienyl)-1-methylethyl]-1-trimethylsilylbenzene, 6-tert.-

butyl-1,4-dimethoxy-2-[1-(2,3,4,5-tetramethylcyclopenta-
 1,4-dienyl)-1-methylethyl]benzene, 5-tert.-butyl-1-chloro-
 4-methoxy-3-[1-(2,3,4,5-tetramethylcyclopenta-1,4-dienyl)-
 1-methylethyl]benzene, 6-tert.-butyl-1-methoxy-2-[1-
 5 (2,3,4,5-tetramethylcyclopenta-1,4-dienyl)-1-
 methylethyl]benzene,
 1-methoxy-2-[1-(3-trimethylsilylcyclopenta-1,4-dienyl)-1-
 methylethyl]benzene, 1-methoxy-4,6-dimethyl-2-[1-(3-
 trimethylsilylcyclopenta-1,4-dienyl)-1-methylethyl]benzene,
 10 6-tert.-butyl-1-methoxy-4-methyl-2-[1-(3-
 trimethylsilylcyclopenta-1,4-dienyl)-1-methylethyl]benzene,
 1-methoxy-2-phenyl-6-[1-(3-trimethylsilylcyclopenta-1,4-
 dienyl)-1-methylethyl]benzene, 1-tert.-butyldimethylsilyl-
 2-methoxy-5-methyl-3-[1-(3-trimethylsilylcyclopenta-1,4-
 15 dienyl)-1-methylethyl]benzene, 2-methoxy-5-methyl-1-
 trimethylsilyl-3-[1-(3-trimethylsilylcyclopenta-1,4-
 dienyl)-1-methylethyl]benzene, 6-tert.-butyl-1,4-dimethoxy-
 2-[1-(3-trimethylsilylcyclopenta-1,4-dienyl)-1-
 methylethyl]benzene, 5-tert.-butyl-1-chloro-4-methoxy-3-[1-
 20 (3-trimethylsilylcyclopenta-1,4-dienyl)-1-
 methylethyl]benzene, 6-tert.-butyl-1-methoxy-2-[1-(3-
 trimethylsilylcyclopenta-1,4-dienyl)-1-methylethyl]benzene,
 2-[1-(cyclopenta-1,4-dienyl)-1-ethylpropyl]-1-
 methoxybenzene, 2-[1-(cyclopenta-1,4-dienyl)-1-
 25 ethylpropyl]-1-methoxy-4,6-dimethylbenzene, 6-tert.-butyl-
 2-[1-(cyclopenta-1,4-dienyl)-1-ethylpropyl]-1-methoxy-4-
 methylbenzene, 6-[1-(cyclopenta-1,4-dienyl)-1-ethylpropyl]-
 1-methoxy-2-phenylbenzene, 1-tert.-butyldimethylsilyl-3-[1-
 (cyclopenta-1,4-dienyl)-1-ethylpropyl]-2-methoxy-5-

methylbenzene, 3-[1-(cyclopenta-1,4-dienyl)-1-ethylpropyl]-
 2-methoxy-5-methyl-1-trimethylsilylbenzene, 6-tert.-butyl-
 2-[1-(cyclopenta-1,4-dienyl)-1-ethylpropyl]-1,4-
 dimethoxybenzene, 5-tert.-butyl-1-chloro-3-[1-(cyclopenta-
 1,4-dienyl)-1-ethylpropyl]-4-methoxybenzene, 6-tert.-butyl-
 2-[1-(cyclopenta-1,4-dienyl)-1-ethylpropyl]-1-
 methoxybenzene,
 2-[1-(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]-1-
 methoxybenzene, 2-[1-(cyclopenta-1,4-dienyl)-1,1-
 diphenylmethyl]-1-methoxy-4,6-dimethylbenzene, 6-tert.-
 butyl-2-[1-(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]-1-
 methoxy-4-methylbenzene, 2-[1-(cyclopenta-1,4-dienyl)-1,1-
 diphenylmethyl]-1-methoxy-6-phenylbenzene, 1-tert.-
 butyldimethylsilyl-3-[1-(cyclopenta-1,4-dienyl)-1,1-
 diphenylmethyl]-2-methoxy-5-methylbenzene, 3-[(cyclopenta-
 1,4-dienyl)-1,1-diphenylmethyl]-2-methoxy-5-methyl-1-
 trimethylsilylbenzene, 6-tert.-butyl-2-[(cyclopenta-1,4-
 dienyl)-1,1-diphenylmethyl]-1,4-dimethoxybenzene, 5-tert.-
 butyl-1-chloro-3-[(cyclopenta-1,4-dienyl)-1,1-
 diphenylmethyl]-4-methoxybenzene, 6-tert.-butyl-2-
 [(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]-1-
 methoxybenzene,
 1-allyloxy-2-[(cyclopenta-1,4-dienyl)methyl]benzene, 1-
 allyloxy-2-[(cyclopenta-1,4-dienyl)methyl]-4,6-
 dimethylbenzene, 1-allyloxy-2-tert.-butyl-6-[(cyclopenta-
 1,4-dienyl)methyl]-4-methylbenzene, 1-allyloxy-6-
 [(cyclopenta-1,4-dienyl)methyl]-2-phenylbenzene, 2-
 allyloxy-1-tert.-butyldimethylsilyl-3-[(cyclopenta-1,4-
 dienyl)methyl]-5-methylbenzene, 2-allyloxy-3-[(cyclopenta-

- 1,4-dienyl)methyl]-5-methyl-1-trimethylsilylbenzene, 1-allyloxy-2-tert.-butyl-6-[(cyclopenta-1,4-dienyl)methyl]-4-methoxybenzene, 4-allyloxy-3-tert.-butyl-1-chloro-5-[(cyclopenta-1,4-dienyl)methyl]benzene, 1-allyloxy-2-tert.-
- 5 butyl-6-[(cyclopenta-1,4-dienyl)methyl]benzene, 1-allyloxy-2-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-allyloxy-2-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]-4,6-dimethylbenzene, 1-allyloxy-6-tert.-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]-4-
- 10 methylbenzene, 1-allyloxy-6-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]-2-phenylbenzene, 2-allyloxy-1-tert.-butyldimethylsilyl-3-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]-5-methylbenzene, 2-allyloxy-3-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]-5-methyl-1-trimethylsilylbenzene,
- 15 1-allyloxy-6-tert.-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]-4-methoxybenzene, 4-allyloxy-5-tert.-butyl-1-chloro-3-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-allyloxy-6-tert.-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-methylethyl]benzene,
- 20 1-allyloxy-2-[1-(4-methylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-allyloxy-4,6-dimethyl-2-[1-(4-methylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-allyloxy-6-tert.-butyl-4-methyl-2-[1-(4-methylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-allyloxy-6-[1-(4-
- 25 methylcyclopenta-1,4-dienyl)-1-methylethyl]-2-phenylbenzene, 2-allyloxy-1-tert.-butyldimethylsilyl-5-methyl-3-[1-(4-methylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 2-allyloxy-5-methyl-3-[1-(4-methylcyclopenta-1,4-dienyl)-1-methylethyl]-1-trimethylsilylbenzene, 1-allyloxy-6-tert.-

butyl-4-methoxy-2-[1-(4-methylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 4-allyloxy-5-tert.-butyl-1-chloro-3-[1-(4-methylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-allyloxy-6-tert.-butyl-2-[1-(4-methylcyclopenta-1,4-
 5 dienyl)-1-methylethyl]benzene, 1-allyloxy-2-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-allyloxy-2-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]-4,6-dimethylbenzene, 1-allyloxy-6-tert.-butyl-2-[1-(4-tert.-
 10 butylcyclopenta-1,4-dienyl)-1-methylethyl]-4-methylbenzene, 1-allyloxy-6-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]-2-phenylbenzene, 2-allyloxy-1-tert.-butyldimethylsilyl-3-[1-(4-tert.-butylcyclopenta-1,4-
 15 dienyl)-1-methylethyl]-5-methylbenzene, 2-allyloxy-3-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]-5-methyl-1-trimethylsilylbenzene, 1-allyloxy-6-tert.-butyl-2-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]-4-
 methoxybenzene, 4-allyloxy-5-tert.-butyl-1-chloro-3-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-
 20 allyloxy-6-tert.-butyl-2-[1-(4-tert.-butylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-allyloxy-2-[1-(2,3,4,5-tetramethylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-allyloxy-4,6-dimethyl-2-[1-(2,3,4,5-tetramethylcyclopenta-1,4-dienyl)-1-
 25 methylethyl]benzene, 1-allyloxy-6-tert.-butyl-4-methyl-2-[1-(2,3,4,5-tetramethylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-allyloxy-2-phenyl-6-[1-(2,3,4,5-tetramethylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 2-allyloxy-1-tert.-butyldimethylsilyl-5-methyl-3-[1-(2,3,4,5-

- tetramethylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 2-allyloxy-5-methyl-3-[1-(2,3,4,5-tetramethylcyclopenta-1,4-dienyl)-1-methylethyl]-1-trimethylsilylbenzene, 1-allyloxy-6-tert.-butyl-4-methoxy-2-[1-(2,3,4,5-
- 5 tetramethylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 4-allyloxy-5-tert.-butyl-1-chloro-3-[1-(2,3,4,5-
- tetramethylcyclopenta-1,4-dienyl)-1-methylethyl]benzene, 1-allyloxy-6-tert.-butyl-2-[1-(2,3,4,5-tetramethylcyclopenta-
- 1,4-dienyl)-1-methylethyl]benzene,
- 10 1-allyloxy-2-[1-(3-trimethylsilylcyclopenta-1,4-dienyl)-1-
- methylethyl]benzene, 1-allyloxy-4,6-dimethyl-2-[1-(3-
- trimethylsilylcyclopenta-1,4-dienyl)-1-methylethyl]benzene,
- 1-allyloxy-6-tert.-butyl-4-methyl-2-[1-(3-
- trimethylsilylcyclopenta-1,4-dienyl)-1-methylethyl]benzene,
- 15 1-allyloxy-2-phenyl-6-[1-(3-trimethylsilylcyclopenta-1,4-
- dienyl)-1-methylethyl]benzene, 2-allyloxy-1-tert.-
- butyldimethylsilyl-5-methyl-3-[1-(3-
- trimethylsilylcyclopenta-1,4-dienyl)-1-methylethyl]benzene,
- 2-allyloxy-5-methyl-1-trimethylsilyl-3-[1-(3-
- 20 trimethylsilylcyclopenta-1,4-dienyl)-1-methylethyl]benzene,
- 1-allyloxy-6-tert.-butyl-4-methoxy-2-[1-(3-
- trimethylsilylcyclopenta-1,4-dienyl)-1-methylethyl]benzene,
- 4-allyloxy-5-tert.-butyl-1-chloro-3-[1-(3-
- trimethylsilylcyclopenta-1,4-dienyl)-1-methylethyl]benzene,
- 25 1-allyloxy-6-tert.-butyl-2-[1-(3-trimethylsilylcyclopenta-
- 1,4-dienyl)-1-methylethyl]benzene,
- 1-allyloxy-2-[1-(cyclopenta-1,4-dienyl)-1-
- ethylpropyl]benzene, 1-allyloxy-2-[1-(cyclopenta-1,4-
- dienyl)-1-ethylpropyl]-4,6-dimethylbenzene, 1-allyloxy-6-

tert.-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-ethylpropyl]-4-methylbenzene, 1-allyloxy-6-[1-(cyclopenta-1,4-dienyl)-1-ethylpropyl]-2-phenylbenzene, 2-allyloxy-1-tert.-butyldimethylsilyl-3-[1-(cyclopenta-1,4-dienyl)-1-ethylpropyl]-5-methylbenzene, 2-allyloxy-3-[1-(cyclopenta-1,4-dienyl)-1-ethylpropyl]-5-methyl-1-trimethylsilylbenzene, 1-allyloxy-6-tert.-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-ethylpropyl]-4-methoxybenzene, 4-allyloxy-5-tert.-butyl-1-chloro-3-[1-(cyclopenta-1,4-dienyl)-1-ethylpropyl]benzene, 1-allyloxy-6-tert.-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-ethylpropyl]benzene, 1-allyloxy-2-[1-(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]benzene, 1-allyloxy-2-[1-(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]-4,6-dimethylbenzene, 1-allyloxy-6-tert.-butyl-2-[1-(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]-4-methylbenzene, 1-allyloxy-2-[1-(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]-6-phenylbenzene, 2-allyloxy-1-tert.-butyldimethylsilyl-3-[1-(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]-5-methylbenzene, 2-allyloxy-3-[(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]-5-methyl-1-trimethylsilylbenzene, 1-allyloxy-6-tert.-butyl-2-[(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]-4-methoxybenzene, 4-allyloxy-5-tert.-butyl-1-chloro-3-[(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]benzene, 1-allyloxy-6-tert.-butyl-2-[(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]benzene, and analogous compounds to the above compounds in which a methoxy or an allyloxy group is replaced by an ethoxy group, a benzyloxy group, a trimethylsilyloxy group, a tert.-butyldimethylsilyloxy

group or a methoxymethoxy group; or a cyclopenta-1,4-dienyl group is replaced by a dimethylcyclopenta-1,4-dienyl group, a trimethylcyclopenta-1,4-dienyl group, a n-butylcyclopenta-1,4-dienyl group, a tert.-

5 butyldimethylsilylcyclopenta-1,4-dienyl group, an indenyl group or a fluorenyl group; or a 1-methoxybenzene group is replaced by a 1-methoxy-6-methylbenzene group, 1-methoxy-4,6-di-tert.-butylbenzene group, a 1-methoxy-4-methyl-6-phenylbenzene group, a 1-tert.-butyldimethylsilyl-2-methoxybenzene group or a 2-methoxy-1-trimethylsilylbenzene group; and further,

(cyclopenta-1,3-dienyl) (2-methoxyphenyl) dimethylsilane,

(cyclopenta-1,3-dienyl) (2-methoxy-3-

methylphenyl) dimethylsilane, (cyclopenta-1,3-dienyl) (2-

15 methoxy-3,5-dimethylphenyl) dimethylsilane, (3-tert.-butyl-

2-methoxyphenyl) (cyclopenta-1,3-dienyl) dimethylsilane, (3-

tert.-butyl-2-methoxy-5-methylphenyl) (cyclopenta-1,3-

dienyl) dimethylsilane, (3,5-di-tert.-butyl-2-

methoxyphenyl) (cyclopenta-1,3-dienyl) dimethylsilane,

20 (cyclopenta-1,3-dienyl) (2-methoxy-5-methyl-3-

phenylphenyl) dimethylsilane, (cyclopenta-1,3-dienyl) (2-

methoxy-5-methyl-3-trimethylsilylphenyl) dimethylsilane, (3-

tert.-butyldimethylsilyl-2-methoxy-5-

methylphenyl) (cyclopenta-1,3-dienyl) dimethylsilane, (3,5-

25 diamyl-2-methoxyphenyl) (cyclopenta-1,3-

dienyl) dimethylsilane, (3-tert.-butyl-2,5-

dimethoxyphenyl) (cyclopenta-1,3-dienyl) dimethylsilane, (5-

tert.-butyl-3-chloro-6-methoxyphenyl) (cyclopenta-1,3-

dienyl) dimethylsilane,

- (2-methoxyphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane,
 (2-methoxy-3-methylphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (2-methoxy-3,5-dimethylphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane,
 5 (3-tert.-butyl-2-methoxyphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (3-tert.-butyl-2-methoxy-5-methylphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane,
 (3,5-di-tert.-butyl-2-methoxyphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (2-methoxy-5-methyl-3-phenylphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane,
 10 (2-methoxy-5-methyl-3-trimethylsilylphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (3-tert.-butyldimethylsilyl-2-methoxy-5-methylphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane,
 15 (3,5-diamyl-2-methoxyphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (3-tert.-butyl-2,5-dimethoxyphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane,
 (5-tert.-butyl-3-chloro-6-methoxyphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane,
 20 (2-methoxyphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-methoxy-3-methylphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane,
 (2-methoxy-3,5-dimethylphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (3-tert.-butyl-2-methoxyphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane,
 25 (3-tert.-butyl-2-methoxy-5-methylphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (3,5-di-tert.-butyl-2-

- methoxyphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-methoxy-5-methyl-3-phenylphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-methoxy-5-methyl-3-trimethylsilylphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (3-tert.-butyldimethylsilyl-2-methoxy-5-methylphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (3,5-diamyl-2-methoxyphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (3-tert.-butyl-2,5-dimethoxyphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (5-tert.-butyl-3-chloro-6-methoxyphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane,
- (tert.-butylcyclopenta-1,3-dienyl) (2-methoxyphenyl)dimethylsilane, (tert.-butylcyclopenta-1,3-dienyl) (2-methoxy-3-methylphenyl)dimethylsilane, (tert.-butylcyclopenta-1,3-dienyl) (2-methoxy-3,5-dimethylphenyl)dimethylsilane, (tert.-butylcyclopenta-1,3-dienyl) (3-tert.-butyl-2-methoxyphenyl)dimethylsilane, (tert.-butylcyclopenta-1,3-dienyl) (3-tert.-butyl-2-methoxy-5-methylphenyl)dimethylsilane, (tert.-butylcyclopenta-1,3-dienyl) (3,5-di-tert.-butyl-2-methoxyphenyl)dimethylsilane, (tert.-butylcyclopenta-1,3-dienyl) (2-methoxy-5-methyl-3-phenylphenyl)dimethylsilane, (tert.-butylcyclopenta-1,3-dienyl) (2-methoxy-5-methyl-3-trimethylsilylphenyl)dimethylsilane, (tert.-butylcyclopenta-1,3-dienyl) (3-tert.-butyldimethylsilyl-2-methoxy-5-methylphenyl)dimethylsilane, (3,5-diamyl-2-

methoxyphenyl) (tert.-butylcyclopenta-1,3-
dienyl)dimethylsilane, (tert.-butylcyclopenta-1,3-
dienyl) (3-tert.-butyl-2,5-dimethoxyphenyl)dimethylsilane,
(5-tert.-butyl-3-chloro-6-methoxyphenyl) (tert.-
5 butylcyclopenta-1,3-dienyl) dimethylsilane,
(2-methoxyphenyl) (trimethylsilylcyclopenta-1,3-
dienyl)dimethylsilane, (2-methoxy-3-
methylphenyl) (trimethylsilylcyclopenta-1,3-
dienyl)dimethylsilane, (2-methoxy-3,5-
10 dimethylphenyl) (trimethylsilylcyclopenta-1,3-
dienyl)dimethylsilane, (3-tert.-butyl-2-
methoxyphenyl) (trimethylsilylcyclopenta-1,3-
dienyl)dimethylsilane, (3-tert.-butyl-2-methoxy-5-
methylphenyl) (trimethylsilylcyclopenta-1,3-
15 dienyl)dimethylsilane,
(3,5-di-tert.-butyl-2-
methoxyphenyl) (trimethylsilylcyclopenta-1,3-
dienyl)dimethylsilane, (2-methoxy-5-methyl-3-
phenylphenyl) (trimethylsilylcyclopenta-1,3-
20 dienyl)dimethylsilane, (2-methoxy-5-methyl-3-
trimethylsilylphenyl) (trimethylsilylcyclopenta-1,3-
dienyl)dimethylsilane, (3-tert.-butyldimethylsilyl-2-
methoxy-5-methylphenyl) (trimethylsilylcyclopenta-1,3-
dienyl)dimethylsilane, (3,5-diamyl-2-
25 methoxyphenyl) (trimethylsilylcyclopenta-1,3-
dienyl)dimethylsilane, (3-tert.-butyl-2,5-
dimethoxyphenyl) (trimethylsilylcyclopenta-1,3-
dienyl)dimethylsilane, (5-tert.-butyl-3-chloro-6-
methoxyphenyl) (trimethylsilylcyclopenta-1,3-

dienyl)dimethylsilane,

(inden-1-yl)(2-methoxyphenyl)dimethylsilane, (inden-2-yl)(2-methoxyphenyl)dimethylsilane, (inden-1-yl)(2-methoxy-3-methylphenyl)dimethylsilane, (inden-2-yl)(2-methoxy-3-

5 methylphenyl)dimethylsilane, (inden-1-yl)(2-methoxy-3,5-dimethylphenyl)dimethylsilane, (inden-2-yl)(2-methoxy-3,5-dimethylphenyl)dimethylsilane, (3-tert.-butyl-2-

methoxyphenyl)(inden-1-yl)dimethylsilane, (3-tert.-butyl-2-methoxyphenyl)(inden-2-yl)dimethylsilane, (3-tert.-butyl-2-

10 methoxy-5-methylphenyl)(inden-1-yl)dimethylsilane, (3-tert.-butyl-2-methoxy-5-methylphenyl)(inden-2-yl)dimethylsilane, (3,5-di-tert.-butyl-2-

methoxyphenyl)(inden-1-yl)dimethylsilane, (3,5-di-tert.-butyl-2-methoxyphenyl)(inden-2-yl)dimethylsilane, (inden-1-

15 yl)(2-methoxy-5-methyl-3-phenylphenyl)dimethylsilane, (inden-2-yl)(2-methoxy-5-methyl-3-

phenylphenyl)dimethylsilane, (inden-1-yl)(2-methoxy-5-methyl-3-trimethylsilylphenyl)dimethylsilane, (inden-2-yl)(2-methoxy-5-methyl-3-

20 trimethylsilylphenyl)dimethylsilane, (3-tert.-butyl-2-methoxy-5-methylphenyl)(inden-1-yl)dimethylsilane, (3-tert.-butyl-2-methoxy-5-methylphenyl)(inden-2-

yl)dimethylsilane, (3,5-diamyl-2-methoxyphenyl)(inden-1-yl)dimethylsilane, (3,5-diamyl-2-methoxyphenyl)(inden-2-

25 yl)dimethylsilane, (3-tert.-butyl-2,5-

dimethoxyphenyl)(inden-1-yl)dimethylsilane, (3-tert.-butyl-2,5-dimethoxyphenyl)(inden-2-yl)dimethylsilane, (5-tert.-

butyl-3-chloro-6-methoxyphenyl)(inden-1-yl)dimethylsilane,

(5-tert.-butyl-3-chloro-6-methoxyphenyl)(inden-2-

- yl)dimethylsilane,
 (9H-fluoren-9-yl) (2-methoxyphenyl)dimethylsilane, (9H-
 fluoren-9-yl) (2-methoxy-3-methylphenyl)dimethylsilane, (9H-
 fluoren-9-yl) (2-methoxy-3,5-dimethylphenyl)dimethylsilane,
 5 (3-tret.-butyl-2-methoxyphenyl) (9H-fluoren-9-
 yl)dimethylsilane, (3-tret.-butyl-2-methoxy-5-
 methylphenyl) (9H-fluoren-9-yl)dimethylsilane, (3,5-di-
 tret.-butyl-2-methoxyphenyl) (9H-fluoren-9-yl)dimethylsilane,
 (9H-fluoren-9-yl) (2-methoxy-5-methyl-3-
 10 phenylphenyl)dimethylsilane, (9H-fluoren-9-yl) (2-methoxy-5-
 methyl-3-trimethylsilylphenyl)dimethylsilane, (3-tret.-
 butyldimethylsilyl-2-methoxy-5-methylphenyl) (9H-fluoren-9-
 yl)dimethylsilane, (3,5-diamyl-2-methoxyphenyl) (9H-fluoren-
 9-yl)dimethylsilane, (3-tret.-butyl-2,5-
 15 dimethoxyphenyl) (9H-fluoren-9-yl)dimethylsilane, (5-tret.-
 butyl-3-chloro-6-methoxyphenyl) (9H-fluoren-9-
 yl)dimethylsilane,
 (2-allyloxyphenyl) (cyclopenta-1,3-dienyl)dimethylsilane,
 (2-allyloxy-3-methylphenyl) (cyclopenta-1,3-
 20 dienyl)dimethylsilane, (2-allyloxy-3,5-
 dimethylphenyl) (cyclopenta-1,3-dienyl)dimethylsilane, (2-
 allyloxy-3-tert.-butylphenyl) (cyclopenta-1,3-
 dienyl)dimethylsilane, (2-allyloxy-3-tert.-butyl-5-
 methylphenyl) (cyclopenta-1,3-dienyl)dimethylsilane, (2-
 25 allyloxy-3,5-di-tert.-butylphenyl) (cyclopenta-1,3-
 dienyl)dimethylsilane, (2-allyloxy-5-methyl-3-
 phenylphenyl) (cyclopenta-1,3-dienyl)dimethylsilane, (2-
 allyloxy-5-methyl-3-trimethylsilylphenyl) (cyclopenta-1,3-
 dienyl)dimethylsilane, (2-allyloxy-3-tert.-

- butyldimethylsilyl-5-methylphenyl) (cyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-diamylphenyl) (cyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert.-butyl-5-methoxyphenyl) (cyclopenta-1,3-dienyl)dimethylsilane, (6-allyloxy-5-tert.-butyl-3-chlorophenyl) (cyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxyphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-methylphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-dimethylphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert.-butylphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert.-butyl-5-methylphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-di-tert.-butylphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-5-methyl-3-phenylphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-5-methyl-3-trimethylsilylphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert.-butyldimethylsilyl-5-methylphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-diamylphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert.-butyl-5-methoxyphenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (6-allyloxy-5-tert.-butyl-3-chlorophenyl) (methylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxyphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-methylphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-

- allyloxy-3,5-dimethylphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert.-butylphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert.-butyl-5-methylphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-di-tert.-butylphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-5-methyl-3-phenylphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-5-methyl-3-trimethylsilylphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert.-butyldimethylsilyl-5-methylphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-diamylphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert.-butyl-5-methoxyphenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (6-allyloxy-5-tert.-butyl-3-chlorophenyl) (2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane,
- (2-allyloxyphenyl) (tert.-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-methylphenyl) (tert.-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-dimethylphenyl) (tert.-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert.-butylphenyl) (tert.-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert.-butyl-5-methylphenyl) (tert.-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-di-tert.-

- butylphenyl) (tert.-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-5-methyl-3-phenylphenyl) (tert.-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-5-methyl-3-trimethylsilylphenyl) (tert.-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert.-butyldimethylsilyl-5-methylphenyl) (tert.-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-dimethylphenyl) (tert.-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert.-butyl-5-methoxyphenyl) (tert.-butylcyclopenta-1,3-dienyl)dimethylsilane, (6-allyloxy-5-tert.-butyl-3-chlorophenyl) (tert.-butylcyclopenta-1,3-dienyl)dimethylsilane,
- (2-allyloxyphenyl) (trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-methylphenyl) (trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-dimethylphenyl) (trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert.-butylphenyl) (trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert.-butyl-5-methylphenyl) (trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-di-tert.-butylphenyl) (trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-5-methyl-3-phenylphenyl) (trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-5-methyl-3-trimethylsilylphenyl) (trimethylsilylcyclopenta-1,3-

25

1-yl)dimethylsilane, (2-allyloxy-3-tert.-
 butyldimethylsilyl-5-methylphenyl)(inden-2-
 yl)dimethylsilane, (2-allyloxy-3,5-diamylphenyl)(inden-1-
 yl)dimethylsilane, (2-allyloxy-3,5-diamylphenyl)(inden-2-
 5 yl)dimethylsilane, (2-allyloxy-3-tert.-butyl-5-
 methoxyphenyl)(inden-1-yl)dimethylsilane, (2-allyloxy-3-
 tert.-butyl-5-methoxyphenyl)(inden-2-yl)dimethylsilane, (6-
 allyloxy-5-tert.-butyl-3-chlorophenyl)(inden-1-
 yl)dimethylsilane, (6-allyloxy-5-tert.-butyl-3-
 10 chlorophenyl)(inden-2-yl)dimethylsilane,
 (2-allyloxyphenyl)(9H-fluoren-9-yl)dimethylsilane, (2-
 allyloxy-3-methylphenyl)(9H-fluoren-9-yl)dimethylsilane,
 (2-allyloxy-3,5-dimethylphenyl)(9H-fluoren-9-
 yl)dimethylsilane, (2-allyloxy-3-tert.-butylphenyl)(9H-
 15 fluoren-9-yl)dimethylsilane, (2-allyloxy-3-tert.-butyl-5-
 methylphenyl)(9H-fluoren-9-yl)dimethylsilane, (2-allyloxy-
 3,5-di-tert.-butylphenyl)(9H-fluoren-9-yl)dimethylsilane,
 (2-allyloxy-5-methyl-3-phenylphenyl)(9H-fluoren-9-
 yl)dimethylsilane, (2-allyloxy-5-methyl-3-
 20 trimethylsilylphenyl)(9H-fluoren-9-yl)dimethylsilane, (2-
 allyloxy-3-tert.-butyldimethylsilyl-5-methylphenyl)(9H-
 fluoren-9-yl)dimethylsilane, (2-allyloxy-3,5-
 diamylphenyl)(9H-fluoren-9-yl)dimethylsilane, (2-allyloxy-
 3-tert.-butyl-5-methoxyphenyl)(9H-fluoren-9-
 25 yl)dimethylsilane, (6-allyloxy-5-tert.-butyl-3-
 chlorophenyl)(9H-fluoren-9-yl)dimethylsilane, (1-
 allyloxynaphthalen-2-yl)dimethyl(1,2,3,4-
 tetramethylcyclopentadienyl)silane, etc.

analogous compounds to the above compounds in which a

methoxy or an allyloxy group is replaced by a benzyloxy group, an ethoxy group, a trimethylsilyloxy group, a tert.-butyldimethylsilyloxy group or a methoxymethoxy group; or a dimethylsilane group is replaced by a diethylsilane group, a diphenylsilane group or a dimethoxysilane group; or a cyclopentadienyl group is replaced by a dimethylcyclopentadienyl group, a trimethylcyclopentadienyl group, a n-propylcyclopentadienyl group, an isopropylcyclopentadienyl group, a n-butylcyclopentadienyl group, an isobutylcyclopentadienyl group, a sec.-butylcyclopentadienyl group, a tert.-butyldimethylsilylcyclopentadienyl group, a phenylcyclopentadienyl group or a methylindenyl group; or a 2-methoxyphenyl group is replaced by a 3-phenyl-2-methoxyphenyl group, a 3-trimethylsilyl-2-methoxyphenyl group or a 3-tert.-butyldimethylsilyl-2-methoxyphenyl group.

Such compounds (3) may contain a plurality of isomers which are due to the positions of substituents and/or the positions of double bonds in a cyclopentadiene moiety of the substituent Cp. The compound (3) of the present invention includes all such isomers.

Industrial Applicability

According to the processes of the present invention, a wide variety of cyclopentadienyl metal salts and also the derivatives of cyclopentadiene can be prepared at a high conversion and a high selectivity without the use of expensive reagents and low-temperature facilities.

Examples

The present invention will be illustrated by the

following examples, which do not limit the scope of the invention in any way.

Example 1

5 Tetramethylcyclopentadiene (1.16 g; purity: 86 %; pure compound: 1.00 g) was dissolved in tetrahydrofuran (20 ml). Then, sodium hydride (washed with hexane) (0.197 g) and diisopropylamine (0.0828 g) were added to the solution, followed by refluxing for 7 hours.

10 After cooling the reaction mixture to room temperature, dichlorodimethylsilane (3.16 g) was added to the reaction mixture, and stirred for 30 minutes to convert tetramethylcyclopentadienylsodium to chlorodimethyl(tetramethylcyclopentadienyl)silane. Chlorodimethyl(tetramethylcyclopentadienyl)silane was
15 quantitatively analyzed by gas chromatography, and the yield of tetramethylcyclopentadienylsodium was calculated. The yield was 53 %.

Example 2

20 The same procedures as those in Example 1 were repeated except that 2,2,6,6-tetramethylpiperidine (0.0578 g) was used in place of diisopropylamine, and the refluxing time was changed from 7 hours to 5 hours. The yield of tetramethylcyclopentadienylsodium was 33 %.

Example 3

25 The same procedures as those in Example 1 were repeated except that butylamine (0.0299 g) was used in place of diisopropylamine, and the refluxing time was changed from 7 hours to 5 hours. The yield of tetramethylcyclopentadienylsodium was 18 %.

Comparative Example 1

The same procedures as those in Example 1 were repeated except that no diisopropylamine was used. The yield of tetramethylcyclopentadienylsodium was 0 %.

5 Comparative Example 2

The same procedures as those in Example 1 were repeated except that potassium tert.-butoxide (1.84 g) was used in place of the combination of sodium hydride and diisopropylamine. The yield of
10 tetramethylcyclopentadienylsodium was 0 %.

Example 4

Sodium hydride (containing mineral oil; the content of sodium hydride: 60 %) (0.41 g) and aniline (0.033 g) were added to the solution of tetramethylcyclopentadiene (0.63
15 g) in tetrahydrofuran (15 ml), and stirred at 40°C for 4 hours. Thus, tetramethylcyclopentadienylsodium was obtained in the form of a solution in tetrahydrofuran.

Methyl iodide (2.8 g) was added to the obtained reaction solution, and stirred for 30 minutes to convert
20 tetramethylcyclopentadienylsodium to pentamethylcyclopentadiene. The content of pentamethylcyclopentadiene was 0.62 g, when measured by gas chromatography. Thus, the yield of tetramethylcyclopentadienylsodium was 88 %.

25 Example 5

The same procedures as those in Example 4 were repeated except that potassium hydride (containing mineral oil; the content of potassium hydride: 35 %) (1.17 g) was used in place of sodium hydride. The yield of

tetramethylcyclopentadienylpotassium was 90 %.

Example 6

Sodium hydride (containing mineral oil; the content of sodium hydride: 60 %) (0.80 g) and m-chloroaniline (0.064 g) were added to the solution of tetramethylcyclopentadiene (1.34 g; purity: 91.3 %; pure compound: 1.22 g) dissolved in tetrahydrofuran (6.73 g), and stirred at 50°C for one hour. Thus, tetramethylcyclopentadienylsodium was obtained in the form of a solution in tetrahydrofuran.

Methyl iodide (2.8 g) was added to the obtained reaction solution, and stirred for 30 minutes to convert tetramethylcyclopentadienylsodium to pentamethylcyclopentadiene. When the content of pentamethylcyclopentadiene was measured by gas chromatography, the yield of tetramethylcyclopentadienylsodium was 83 %.

Example 7

The same procedures as those in Example 6 were repeated except that cyclopentadiene (0.661 g) was used in place of tetramethylcyclopentadiene, and butylamine (0.037 g) was used in place of m-chloroaniline. The yield of cyclopentadienylsodium was 99 %.

Example 8

Sodium hydride (containing mineral oil; the content of sodium hydride: 60 %) (0.80 g) and aniline (0.046 g) were added to the solution of trimethylcyclopentadiene (1.08 g) dissolved in tetrahydrofuran (6.12 g), and stirred at 50°C for 3 hours. Thus, trimethylcyclopentadienylsodium was obtained in the form of a solution in tetrahydrofuran.

Methyl iodide (2.8 g) was added to the obtained reaction solution, and stirred for 30 minutes to convert trimethylcyclopentadienylsodium to tetramethylcyclopentadiene. When the content of tetramethylcyclopentadiene was measured by gas chromatography, the yield of trimethylcyclopentadienylsodium was 90 %.

Example 9

The same procedures as those in Example 8 were repeated except that 2-cyclopentadienyl-2-fluorenylpropane (2.72 g) was used in place of trimethylcyclopentadiene, the amount of tetrahydrofuran was changed from 6.12 g to 15.4 g, the amount of sodium hydride (containing mineral oil; the content of sodium hydride: 60 %) was changed from 0.80 g to 1.60 g, the amount of aniline was changed from 0.046 g to 0.092 g, and the amount of methyl iodide was changed from 2.8 g to 5.6 g. The yield of 2-cyclopentadienyl-2-fluorenylpropane disodium salt was 93 %.

Example 10

The same procedures as those in Example 8 were repeated except that bistrimethylcyclopentadienyldimethylsilane (2.73 g) was used in place of trimethylcyclopentadiene, the amount of tetrahydrofuran was changed from 6.12 g to 15.5 g, the amount of sodium hydride (containing mineral oil; the content of sodium hydride: 60 %) was changed from 0.80 g to 1.60 g, the amount of aniline was changed from 0.046 g to 0.092 g, and the amount of methyl iodide was changed from 2.8 g to 5.6 g. The yield of bistrimethylcyclopentadienyldimethylsilane disodium salt

was 88 %.

Example 11

The same procedures as those in Example 8 were repeated except that 1,2-bisindenylethane (2.58 g) was used in place of trimethylcyclopentadiene, the amount of tetrahydrofuran was changed from 6.12 g to 14.6 g, the amount of sodium hydride (containing mineral oil; the content of sodium hydride: 60 %) was changed from 0.80 g to 1.60 g, the amount of aniline was changed from 0.046 g to 0.092 g, and the amount of methyl iodide was changed from 2.8 g to 5.6 g. The yield of 1,2-bisindenylethane disodium salt was 92 %.

Example 12

Sodium hydride (containing mineral oil; the content of sodium hydride: 60 %) (3.30 g) and aniline (0.237 g) were added to the solution of tetramethylcyclopentadiene (5.01 g) dissolved in tetrahydrofuran (45 ml), and stirred at 40°C for 4 hours. Thus, tetramethylcyclopentadienylsodium was obtained in the form of a solution in tetrahydrofuran.

Methyl iodide (8.0 g) was added to the obtained reaction solution, and stirred for 30 minutes to convert tetramethylcyclopentadienylsodium to pentamethylcyclopentadiene. The content of pentamethylcyclopentadiene was 4.80 g when measured by gas chromatography. Thus, the yield of tetramethylcyclopentadienylsodium was 86 %.

Example 13

Sodium hydride (containing mineral oil; the content of sodium hydride: 60 %) (2.50 g) and aniline (0.237 g) were

added to the solution of tetramethylcyclopentadiene (5.01 g) dissolved in tetrahydrofuran (28 ml), and stirred at 40°C for 4 hours. Thus, tetramethylcyclopentadienylsodium was obtained in the form of a solution in tetrahydrofuran.

5 Methyl iodide (8.0 g) was added to the obtained reaction solution, and stirred for 30 minutes to convert tetramethylcyclopentadienylsodium to pentamethylcyclopentadiene. The content of pentamethylcyclopentadiene was 4.78 g when measured by gas chromatography. Thus, the yield of
10 tetramethylcyclopentadienylsodium was 85 %.

Example 14

Sodium hydride (containing mineral oil; the content of sodium hydride: 60 wt.%) (0.60 g) was suspended in
15 tetrahydrofuran (6.91 g), and then aniline (0.047 g) was dropwise added to the suspension at 25°C. After heating to 50°C, the suspension was stirred for 10 minutes. Thereafter, tetramethylcyclopentadiene (1.22g) was dropwise added to the suspension while maintaining the suspension at
20 50°C, followed by stirring for one hour. Thus, tetramethylcyclopentadienylsodium was obtained. After cooling the above solution to 20°C, the solution of (2-allyloxy-3-tert.-butyl-5-methylphenyl)chlorodimethylsilane (3.86 g; purity: 73 %; pure compound: 2.82 g) in toluene
25 was dropwise added to the above solution, followed by stirring for 2 hours.

After adding water (3 g) to the reaction mixture, the solvent was evaporated off. Toluene (10 g) and water (3 g) were added to the residual oil, and the mixture was

separated. The organic layer was concentrated, and (2-allyloxy-3-tert.-butyl-5-methylphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane (4.97 g; purity: 63 %; pure compound: 3.13 g) was obtained. The yield was 82 % based on tetramethylcyclopentadiene.

Example 15

Potassium hydride (containing mineral oil; the content of sodium hydride: 35 %) (3.00 g) was suspended in tetrahydrofuran (18 ml), and then 4-methylaniline (0.056 g) was dropwise added to the suspension at 10°C, followed by stirring for 10 minutes. Thereafter, the solution of tetramethylcyclopentadiene (1.22g) dissolved in tetrahydrofuran (6 ml) was dropwise added to the suspension, and heated to 25°C, followed by stirring for one hour. Thus, tetramethylcyclopentadienylpotassium was obtained. To this solution, the solution of (2-allyloxy-3-tert.-butyl-5-methylphenyl)chlorodimethylsilane (3.99 g; purity: 70.7 %; pure compound: 2.82 g) dissolved in tetrahydrofuran (3 ml) was dropwise added, followed by stirring for one hour.

After adding water (15 ml) and hexane (15 ml) to the reaction mixture, the mixture was separated. The organic layer was concentrated, and (2-allyloxy-3-tert.-butyl-5-methylphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane (pure compound: 3.23 g) was obtained. The yield was 85 % based on tetramethylcyclopentadiene.

CLAIMS

1. A process for the preparation of a cyclopentadienyl metal salt comprising the step of reacting a cyclopentadiene and a metal hydride in the presence of an amine compound.

2. A process according to claim 1, wherein said amine compound is a primary amine or a secondary amine.

3. A process according to claim 2, wherein said primary amine is a primary aniline.

4. A process according to any one of claims 1 to 3, wherein an amount of said amine compound is from 0.001 to 2 moles per one mole of said metal hydride.

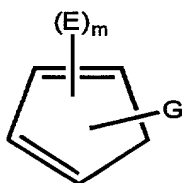
5. A process according to any one of claims 1 to 3, wherein an amount of said amine compound is from 0.01 to 0.5 mole per one mole of said metal hydride.

6. A process according to any one of claims 1 to 5, wherein an amount of said metal hydride is from 0.5 to 3 moles per one mole of said cyclopentadiene.

7. A process according to any one of claims 1 to 6, wherein said metal hydride contains mineral oils.

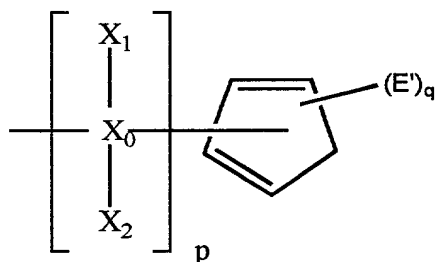
8. A process according to any one of claims 1 to 7, wherein a reaction temperature is from 10 to 60°C.

9. A process according to any one of claims 1 to 8, wherein said cyclopentadiene is a compound of the formula (2a):



wherein m is an integer of 0 to 5, E groups are the same or different and independently represent a C₁-C₈ alkyl group, a phenyl group, a naphthyl group, or a tri-substituted silyl group having substituents selected from the group consisting of a C₁-C₄ alkyl group and a phenyl group, provided that, when two E groups are present on adjacent carbon atoms, they may be bonded at their ends to form a benzene ring, a cyclohexane ring or a cyclohexene ring, which is condensed with the cyclopentadienyl ring,

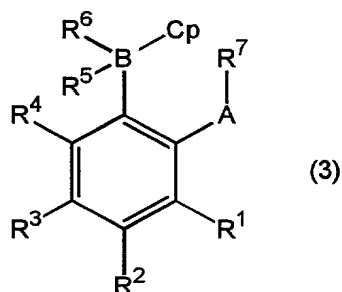
G is a hydrogen atom when m is 5, or when m is 0 to 4, G is a hydrogen atom or a group of the formula (2b):



wherein p is 1 or 2, q is an integer of 0 to 4, X₀ is a carbon atom or a silicon atom, X₁ and X₂ are the same or different and independently represent a hydrogen atom, a C₁-C₄ alkyl group or a phenyl group, E' is a substituent selected from those defined for E, provided that when X₀ is a silicon atom, X₁ and X₂ are not hydrogen atoms.

10. A process according to claim 9, wherein m is an integer of 2 to 5, or m is 1 and G is a group of the formula (2b).

11. A process for the preparation of a cyclopentadiene derivative of the formula (3):



wherein

A is an atom of the 16 group of the Periodic Table,

B is an atom of the 14 group of the Periodic Table,

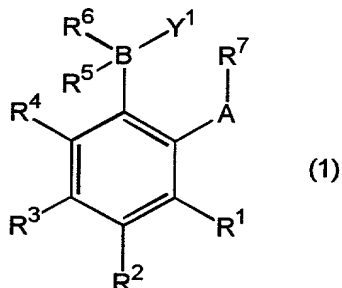
R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are the same or different and independently represent a hydrogen atom, a fluorine atom, a C_1 - C_{20} alkyl group which may optionally be substituted with a fluorine atom, a C_7 - C_{20} aralkyl group which may optionally be substituted with a fluorine atom, a C_6 - C_{20} aryl group which may optionally be substituted with a fluorine atom, a C_1 - C_{20} substituted silyl group, a C_1 - C_{20} alkoxy group which may optionally be substituted with a fluorine atom, a C_7 - C_{20} aralkyloxy group which may optionally be substituted with a fluorine atom, a C_6 - C_{20} aryloxy group which may optionally be substituted with a fluorine atom, or a C_2 - C_{20} di-substituted amino group which may optionally be substituted with a fluorine atom, provided that any two or more of R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may together form a ring,

R^7 is a hydrocarbon group which may optionally be substituted with a fluorine atom, or a tri-substituted silyl group,

and

Cp is a cyclopentadiene ring comprising the step of reacting a halide compound of the

formula (1):



wherein A, B, R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ are the same as defined above, and Y¹ is a chlorine atom, a bromine atom or an iodine atom

with a cyclopentadiene of the formula (2):



wherein Cp is the same as defined above, in the presence of a metal hydride and an amine compound.

12. A process according to claim 11, wherein said cyclopentadiene of the formula (2) is reacted with said metal hydride in the presence of said amine compound, and then reacted with said halide compound of the formula (1).

13. A process according to claim 11 or 12, wherein said cyclopentadiene of the formula (2) is a compound of the formula (2a) in claim 9.

14. A process according to claim 11 or 12, wherein said amine compound is a primary amine or a secondary amine.

15. A process according to claim 14, wherein said primary amine is a primary aniline.

16. A process according to claim 12 to 13, wherein an amount of said amine compound is from 0.001 to 2 moles per one mole of said metal hydride.

17. A process according to claim 12 to 13, wherein an

amount of said amine compound is from 0.01 to 0.5 mole per one mole of said metal hydride.

18. A process according to any one of claims 11 to 13, wherein an amount of said metal hydride is from 0.5 to 3
5 moles per one mole of said compound of the formula (2).

19. A process according to any one of claims 11 to 17, wherein a reaction temperature is from 10 to 60°C.

20. A process according to any one of claims 11 to 19, wherein said metal hydride contains mineral oils.

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ABSTRACT

A cyclopentadienyl metal salt is prepared by reacting a cyclopentadiene and a metal hydride in the presence of an amine compound. Furthermore, a derivative of a
5 cyclopentadiene in which a phenyl group is bonded to its cyclopentadienyl moiety through an element of the 14 group of the Periodic Table is prepared using such a reaction.

00449-039

Declaration and Power of Attorney for Patent Application

特許出願宣言書及び委任状

Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name,

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者(下記の氏名が一つの場合)もしくは最初かつ共同発明者であると(下記の名称が複数の場合)信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

PROCESS FOR THE PREPARATION OF
CYCLOPENTADIENYL METAL SALT AND PROCESS
FOR THE PREPARATION OF DERIVATIVE OF
CYCLOPENTADIENE USING THE SAME

上記発明の明細書(下記の欄でX印がついていない場合は、本書に添付)は、

the specification of which is attached hereto unless the following box is checked:

☐ 月 日に提出され、米国出願番号または特許協定条約

☒ was filed on January 14, 1998
as United States Application Number or
PCT International Application Number

国際出願番号を _____ とし、

PCT/JP98/00110 and was amended on
_____ (if applicable).

(該当する場合) _____ に訂正されました。

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

Japanese Language Declaration

(日本語宣言書)

私は、米国法典第35編第119条(a)-(d)項又は第365条(b)項に基き下記の、米国以外の国の少なくとも一カ国を指定している特許協力条約第365条(a)項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

I hereby claim foreign priority under Title 35, United States Code, Section 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Applications

外国での先行出願

Priority Not Claimed

優先権主張なし

005036/1997	Japan
(Number)	(Country)
(番号)	(国名)
005037/1997	Japan
(Number)	(Country)
(番号)	(国名)
(Number)	(Country)
(番号)	(国名)

14/01/1997	<input type="checkbox"/>
(Day/Month/Year Filed)	
(出願年月日)	
14/01/1997	<input type="checkbox"/>
(Day/Month/Year Filed)	
(出願年月日)	
(Day/Month/Year Filed)	<input type="checkbox"/>
(出願年月日)	

私は、第35編米国法典119条(e)項に基づいて下記の米国特許出願規定に記載された権利をここに主張致します。

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application No.)	(Filing Date)
(出願番号)	(出願日)

(Application No.)	(Filing Date)
(出願番号)	(出願日)

私は、下記の米国法典第35編第120条に基づいて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約第365条(c)に基づく権利をここに主張します。又、本出願の各請求範囲の内容が米国法典第35編第112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内又は特許協力条約国際出願提出日までの期間中に入手された、連邦規則法典第37編第1条第56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

I hereby claim the benefit of Title 35, United States Code Section 120 of any United States application(s), or 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose any material information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

(Application No.)	(Filing Date)
(出願番号)	(出願日)

(Status: Patented, Pending, Abandoned)
(現況: 特許許可済、係属中、放棄済)

(Application No.)	(Filing Date)
(出願番号)	(出願日)

(Status: Patented, Pending, Abandoned)
(現況: 特許許可済、係属中、放棄済)

私は、私自身の知識に基づいて本宣言中で私が行う表明が真実であり、かつ私の入手した情報と私の信ずるところに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行えば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Japanese Language Declaration

(日本語宣言書)

委任状: 私は、下記の発明者として、本出願に関する一切の手続きを米国特許商標局に対して遂行する弁理士又は代理人として、下記のものを指名致します。(弁護士、又は代理人の氏名及び登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (list name and registration number)

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(第三以降の共同発明者についても同様に記載し、署名をする (Supply similar information and signature for third and subsequent joint inventors.)

Japanese Language Declaration

(日本語宣言書)

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第三発明者の署名	日付	Third inventor's signature	Date
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第六発明者の署名	日付	Sixth inventor's signature	Date
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